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ABSTRACT

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The Soviet lag in mass spectral gas analysis is due to lack of equipment. Uses and limitations of the MS-1, MS-2, MS-2M, MS-3 and MS-4 are discussed, leading to extensive evaluation of a new gas analyzer, the MAGS-2. Text and figures give detailed description of instrument.

Author

Mass spectral analysis of gas mixtures has been widely practiced in /35* recent years (refs. 1, 2 and 3). However, application of mass spectral gas analysis on a large scale in Soviet laboratories is lagging because of a lack of the necessary equipment. Soviet industry has produced mass spectrometers for isotopic analysis: the MS-1, MS-2, MS-2M, MS-3 and MS-4. Since these are precision instruments for isotopic analysis, they cannot be used directly for the chemical analysis of gases.

At the same time, mass spectrometers for gas analysis have many structural elements in common with those for isotopic analysis. This fact was used in developing an instrument for analysis of gas and liquid mixtures. The MS-1 mass spectrometer was taken as the basis for the new instrument. The result of this work, which was done jointly by the Institute of Chemical Physics of the Academy of Sciences SSSR and the Scientific Research Institute of the Ministry of the

*Numbers given in margin indicate pagination in original foreign text.

Radio Engineering Industry, was the creation of a mass spectrometer for chemical analysis (ref. 4). We used this instrument as a basis in developing industrial mass spectral analytical instruments which should be available in at least two modifications: in the form of a general purpose analytical mass spectrometer for chemical analysis of gaseous and liquid mixtures of substances with molecular weights up to several hundred atomic mass units, and in the form...^(orig. cut) mixtures of gases with a molecular weight of up to 75-80 atomic mass units.

The finished mass spectral gas analyzer (industrial type MAGS-2, fig. 1) is a united set of equipment containing a single-beam mass spectrometer with a magnetic sector field, a system for admitting the gas mixture to be analyzed into the ion source by molecular inleakage (ref. 5), and a system for automatically recording the mass spectra. The instrument is designed for analyzing

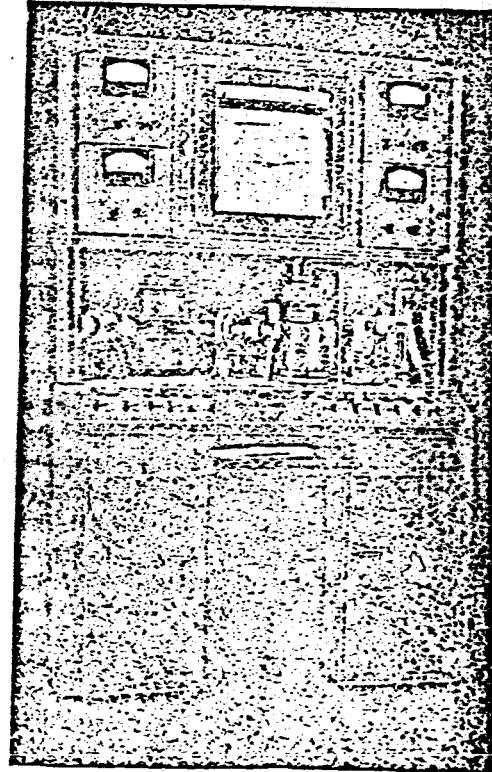


Figure 1. Overall view of the gas analyzer.

gas mixtures with a molecular weight of up to 80 atomic mass units, and may be used in addition for isotopic analysis of chemical elements or compounds which are normally in the gaseous state.

The gas analyzer is fed from an ac electrical system with a linear potential of 380-220 V and requires a power supply of the order of $\frac{1}{2}$ kVa. The overall dimensions of the instrument are $1800 \times 1220 \times 850$ mm.

The sensitivity of the gas analyzer (with respect to CO_2) is 0.01 percent; the accuracy for analysis of a two-component mixture is ± 2 percent relative when the volumetric concentration of the component being determined is no less than 10 percent; the resolving power is 1/80.

The resolving power of the instrument is illustrated in figure 2, which shows the mass spectrum of krypton.

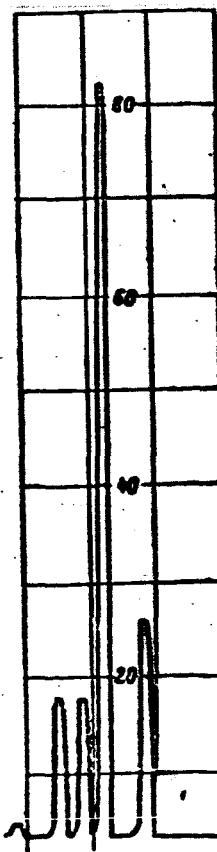


Figure 2. Mass spectrum of krypton.

A block diagram of the gas analyzer is shown in figure 3. Vial 1 with the gas mixture to be analyzed is connected to the copper header of the admission system by a ground joint which has a metal valve equipped with a teflon shutoff element 2. The header is connected by copper tubing to four-way valve 3. The mixture to be analyzed is fed to the pre-evacuated space restricted by tapered copper plugs in three of the shutoffs for valve 3 (shutoffs 4, 5 and 6), and by the mercury surface in a mercury manometer. This manometer may be used to measure a pressure of up to 80 mm Hg with an accuracy of 0.05 mm Hg (the reading is taken with a microscope). After the pressure is measured, the manometer is disconnected from the four-way valve by shutoff 7, and the gas from the "standard" volume formed ($V \approx 8 \text{ cm}^3$) is admitted to two-liter tank 8 which is pre-evacuated to a high vacuum. After admission of the gas into this tank, the pressure of the gas is reduced to 1/250 of what it was in the standard volume and is of the order of 10^{-1} - 10^{-2} mm Hg (depending on the pressure in the standard volume).

Molecular inleakage of the gas takes place through an aluminum diaphragm 8μ thick in which 2-3 holes with a diameter of $10-15 \mu$ have been punched with a needle. This diaphragm is placed between two aluminum discs 0.2 mm thick with a hole 3 mm in diameter in the center. The entire assembly is placed in the flange of inlet valve 9 (see fig. 3). A tapered groove joint¹ is used for making the vacuum seal between the valve flange with its diaphragm assembly and the copper tubing through which the gas is admitted to the ion source.

¹The vacuum system of the gas analyzer is made entirely of metal. All permanent connections are soldered (copper and cadmium solder), while temporary connections are made in the form of joints with tapered grooves and pipe branch joints with a tapered sealing liner.

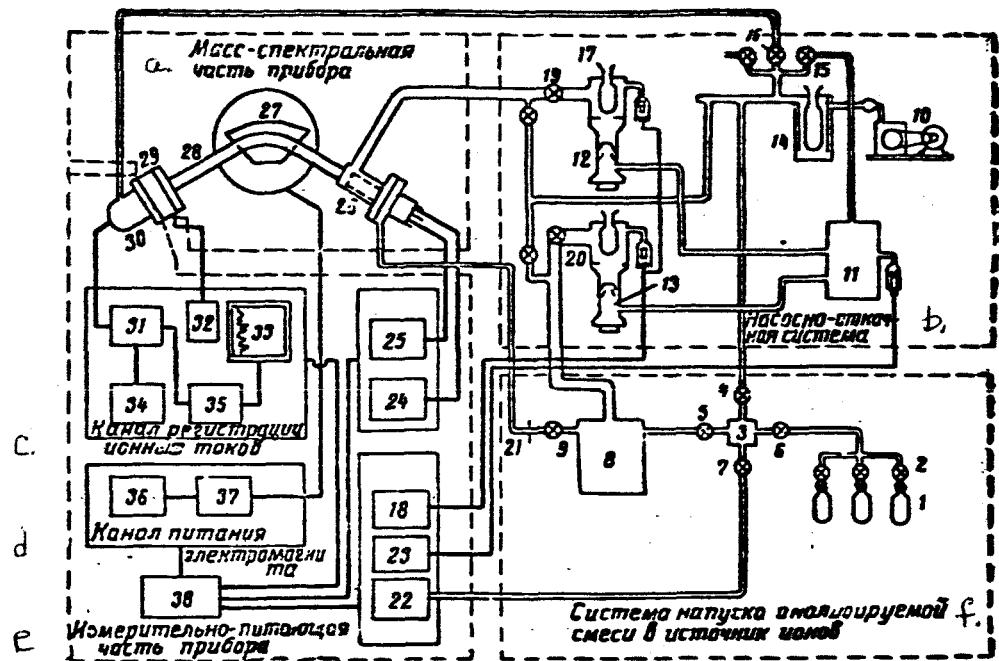


Figure 3. Block diagram of the gas analyzer: 21, inlet diaphragm; 22, mercury manometer; 23, thermocouple manometer; 24, emission stabilizer for ion source cathodes; 25, battery source of acceleration voltage; 26, ion source; 27, electromagnet; 28, chamber; 29, ion receiver; 30, electrometer; 31, dc amplifier with 100 percent negative feedback; 32, suppressor battery; 33, EPP-09 autopotentiometer; 34, amplifier supply regulator; 35, manual recording scale switch; 36, magnet current rectifier; 37, unit for regulation and control of the magnet current; 38, EPA-58 ferroresonance voltage regulator (the remaining components are explained in the text). a, mass spectral part of the instrument; b, vacuum pump system; c, ion current registration channel; d, supply channel for the electromagnet; e, measuring and power supply section of the instrument; f, system for admitting the mixture to be analyzed into the ion source.

The gas admitted to the ion source is ionized by electrons with an energy of 40-100 eV. The cathode emission current is stabilized within ± 1 percent controllable from 0.4 to 2 mA by an electron-magnetic regulator. The potentials to the electrodes of the ion source are supplied from GB-300 dry cells ($V_{acc} = 1500$ V, $V_{dis} \approx 100$ V).

The output beam from the ion source has a rectangular cross section of 8×0.2 mm. This beam then passes into the analyzing chamber. A vacuum pump system is used for maintaining a high vacuum in the chamber ($2 \cdot 10^{-7}$ mm Hg).

The instrument uses a VN-461 mechanical pump as the unit for pre-/37liminary evacuation 10 (see fig. 3). This pump evacuates ballast tank 11, which is connected to mercury vapor pumps. One of these 12 (DRN-10) is used for creating a high vacuum in the chamber, while the other 13 (NR-40) maintains a high vacuum in the inlet tank. Oil vapor trap 14 is placed between the mechanical pump and the ballast tank. The use of a 5 liter ballast tank and shutoff valve 15 makes it possible to operate for several hours while the vacuum pump 10 is disconnected or used for evacuating the inlet system (through shutoff 4 of four-way valve 3) and the bell of the electrometric tube (through cutoff valve 16).

To prevent mercury vapor from entering the chamber and the inlet tank, the diffusion pumps are connected to the chamber and the tank through high-vacuum traps 17 filled with liquid nitrogen. The vacuum is measured by ionization manometers 18 (LM-2) mounted in pipe branches in each of the high-vacuum traps. The chamber and inlet tank are disconnected from the pumping system by all-metal high-vacuum valves 19 and 20. When the magnetic field strength is varied, ions with various m/e ratios are fed sequentially to the collector of the analyzing chamber, in front of which an input slot is mounted. A bellows is used to vary the width of the input slot from 0 to 2 mm. The magnetic field

may be varied manually or automatically. The automatic variation in magnetic field strength (automatic mass spectrum scanning) is exponential (refs. 6 and 7). The entire scanning range is divided into two subranges: the "hydrogen" subrange from 1 to 4 atomic mass units, and the "fundamental" subrange from 12 to 80 atomic mass units. To accelerate scanning in any region of the range, provision is made for reducing the time constant in the discharge circuit of the capacitor which sets the scanning law.

The ion currents arriving at the collector are amplified by an electro-metric dc amplifier with feedback and an input impedance of $\sim 5 \cdot 10^{10} \Omega$. The amplified currents are then recorded on the tape of an EPP-09 self-recording potentiometer, which has a sensitivity of 20 mV, with a carriage motion constant of 1 sec. The recording scales of the potentiometer are switched by a pushbutton voltage divider mounted on the panel of the instrument.¹ This /38 system for scanning and recording mass spectra makes it possible to fix a mass spectrum in the fundamental range (12-80 amu) in 12 min.

The magnetic deflection system in the mass spectral gas analyzer consists of a magnet and an analyzing chamber. Figure 4 shows the magnetic deflection system of the MAGS-2. This system is characterized by the use of second order direction focusing (ref. 8), an angle θ of 30° between the axis of the ion source and the base line, and a central trajectory radius R of 100 mm. The advantages which result from the use of second order aberration correction are illustrated by the data in table 1.

¹G. N. Tager is responsible for development of a number of the electronic units for measurement and power supply used in the instrument.

TABLE 1

Parameter	First order focusing system		System with second order aberration correction	
	General expression	Numerical example for R = 100 mm, θ = 30° and α = 20°20'	General expression	Numerical example for R = 100 mm, θ = 30° and α = 20°20'
Aberration due to the angle of divergence α	$R\alpha^2$	0.17 mm	$AR\alpha^3$	0.024 mm
Base distance (distance from the output slot of the ion source to the collector)	$\frac{2R}{\sin\theta}$	400 mm	$\left[\frac{4}{3} \frac{R}{\sin\theta} + \frac{2}{3} R \sin\theta \right]^{**}$	300 mm
Length of the beam trajectory		451 mm	$\left[c_x = 2R \left(\frac{2}{3} \operatorname{ctg}\theta + \theta \right) \right]^*$	336 mm

*Kerwin (ref. 8) gives an expression for the coordinate of the inflection point of the ideal boundary of the field, where a is half the base distance. On the other hand, $x_f = 2R \sin\theta$. By setting one expression equal to the other, we get the base distance as a function of the radius and the angle θ.

**This expression was derived from simple geometric considerations with regard to Kerwin's equation for the coordinate of the inflection point x_f .

The insignificant ion-optical aberration and reduced overall dimensions of the analyzing chamber give this gas analyzer a higher luminosity than instruments with the same resolving power but with an ordinary magnetic deflection system.

The choice of an angle $\theta = 30^\circ$ is explained by figure 5, where the length of the trajectory of the ion beam is shown as a function of the angle θ. It may

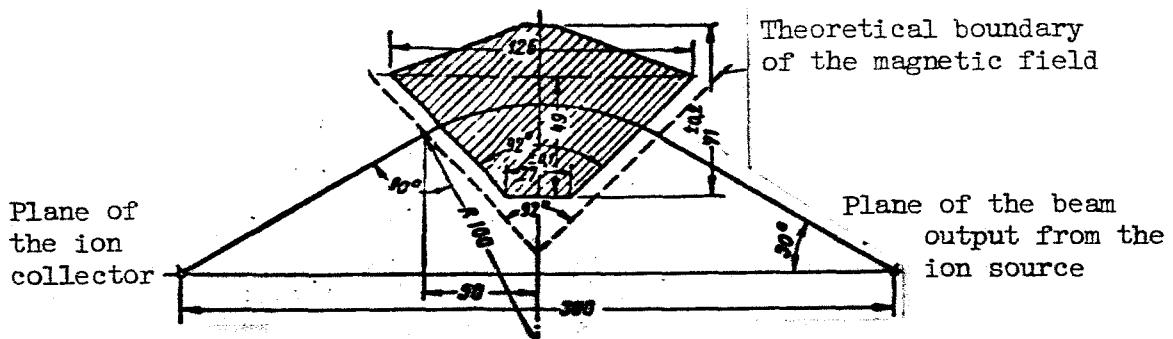


Figure 4. Ion beam magnetic deflection system.

be seen from the graph in this figure that starting at $\theta \approx 30^\circ$ there is little change in the length of the ion beam trajectory with an increase in θ , while /39 the overall dimensions of the magnet increase linearly with an increase in this angle.¹ When $\theta < 30^\circ$ there is a sharp increase in the length of the ion beam trajectory, which results in a number of undesirable consequences.

The resolving power of the gas analyzer is determined by the ordinary formula

$$R_e = \frac{2S_K}{D \cdot R}. \quad (1)$$

where S_K is the width of the reception slot in mm (set equal to the width of the ion beam at the collector); R is the radius of the central trajectory in mm;

¹The area of the pole of the magnet may be expressed as $S = KR\theta$, where K is the proportionality factor determined by the angle of divergence α of the ion beam, and by the height of the air gap between poles. Strictly speaking, analysis has shown that the coefficient K also depends on (missing symbol) for a system with second order aberration correction. However, this dependence is slight, and may be disregarded in the problem of selecting the angle θ .

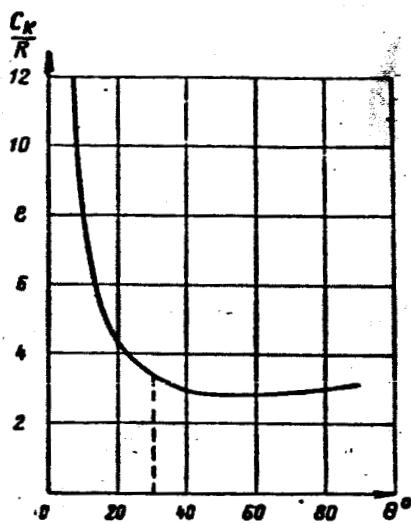


Figure 5. Length of the trajectory of an ion beam $C_K = 2 R [2/3 \operatorname{ctg} \theta + \theta]$ as a function of the angle θ .

D is a coefficient (less than one) which accounts for some reduction in dispersion during focusing with second order aberration correction (ref. 8).

For $S_K = 0.5 \text{ mm}^{**}$, $R = 100 \text{ mm}$, and $D = 0.89$ ($\theta = 30^\circ$), the calculated resolving power is 1/89. As may be seen from figure 2, the actual resolving power is close to theoretical.

The high vacuum trap is among the components which have a considerable effect on the quality of the gas analyzer as an analytical instrument. This is associated with the fact that the gases condensed on the cold surfaces of the

**The width of the slot S_K was determined theoretically taking account of aberrations due to the angle of divergence $\alpha = A R \alpha^3$, and due to deviations of the beam from monochromatic as a result of the ion source, $R \frac{\Delta V}{V}$ (ΔV is the energy scatter of the ions in eV; V is the ionizing voltage). The energy scatter ΔV was taken as $\sim 5 \text{ eV}$.

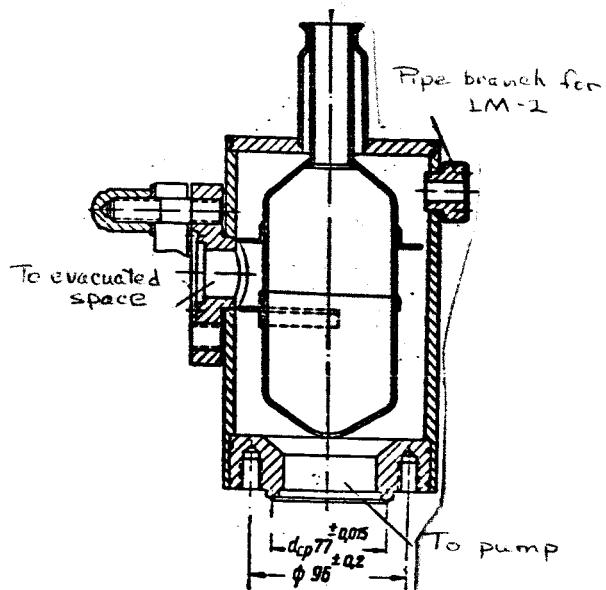


Figure 6. High vacuum trap.

trap may be desorbed as a consequence of heating during subsequent analyses.

When these desorbed gases reach the ionization region, they distort the results of the analyses. This, in particular, is one of the factors responsible for the so-called "memory" of the instrument.

Figure 6 shows a trap design¹ which gives a low instrument "memory."

To reduce the refrigerant consumption and the corresponding retardation in the motion of the edge of the cold zone, the inner reservoir filled with liquid nitrogen is connected to the outer housing by light-gauge double-walled Kovar tubing. When the wall thickness of the tubing is 0.2 mm, the heat conduction is so small that the trap uses only 43 cm³ of liquid nitrogen per hour (the reservoir has a 750 cm³ capacity). However, the most important feature is that the opening of the trap which connects with the evacuated space is turned toward

¹This high vacuum trap was developed by engineers D. B. Zvorikin and G. A. Krysov.

the central section of the inner reservoir where the temperature is nearly constant as the quantity of refrigerant is reduced. On the inside of the reservoir are a reflecting ring and a reflecting semiring which prevent contamination /40 of the ionization region by gases desorbed from the upper part of the reservoir and diffused from the pump. This trap was operationally tested with propane. A 30 percent reduction in the initial level of the refrigerant caused no change in the peaks of the propane spectrum. Similar tests were conducted on the trap of the MS-2M instrument for comparison. The magnitude of the peaks in the propane spectrum increased by 25 percent with the same shift in the coolant level.

Just as in the high vacuum trap, the liquid air-filled inner reservoir in the oil vapor trap is connected by double thin-walled Kovar tubing to the housing. In this design also the low heat conduction of this tubing gives a low consumption of liquid nitrogen ($100 \text{ cm}^3/\text{hr}$) in spite of the comparatively high heat conduction of the intermediate rough vacuum space. The reservoir of the trap has a capacity of 200 cm^3 . The oil vapor trap prevents contamination of the high vacuum region by oil vapor from the mechanical pump, and thus reduces the "background" level of the gas analyzer. This "background" reduction is also achieved by eliminating all seals in the high vacuum region of the instrument which use joint dope, picein, etc. by using electric heaters for degassing the system at very close to 300°C . In addition, a low "background" level is assured by a high vacuum valve with a flow orifice 30 mm in diameter which disconnects the analyzing chamber from the vacuum pump system. Thanks to this, the chamber may always be kept under high vacuum.

A particular feature of the valve design is the inclusion of a small parallel evacuation valve in its housing. This combination eliminates from the high-vacuum region the long parallel evacuation tube which ordinarily interferes with production of the required vacuum purity of the system.

By taking all these measures, the background spectrum of the gas analyzer in the fundamental range (12-80 amu) is reduced to a few lines. The most intense lines are those with $m/e = 18$ (water vapor), 28 (CO) and 44 (CO_2). The intensity of these lines is a few ten-thousandths of that of the mass-spectral lines of the gases which are analyzed. It may be pointed out for comparison that the background spectrum of the MS-1 mass spectrometer, which has no high vacuum valves, is composed of several dozen lines in this same region of mass numbers, with the most intense making up several percent of the peaks of the gases which are analyzed. The residual spectrum of the MS-2M instrument is considerably cleaner. The background spectrum for this mass spectrometer is made up of the same lines as in the gas analyzer, but their relative intensity is approximately three times as great.

The instrument was tested on binary synthetic mixtures. For the sake of simplicity, the components of the mixtures were chosen in such a way that the standard line could be isolated in the mass spectrum of each of them without superposition on the standard line of the other. Data on the errors in analysis for this case may be used to calculate the approximate analytical precision for a mixture of substances with superimposed lines by proper addition of the "weighted" errors. The mixtures were prepared both directly in the inlet system of the gas analyzer and in a separate vacuum installation.

Two methods were used for analysis: the "pressure" method and the "ratio" method. In the first case, the instrument was pregraduated separately for each component of the mixture. Sensitivity to the material k was defined as

(2)

where I_k^0 is the ion current in the maximum of the mass-spectral line taken as standard in the spectrum of the given material, and p_k^0 is the pressure of the given gas in the "standard" volume.

After graduation, a known composition of the mixture to be analyzed was introduced into the analyzer, its mass spectrum was taken, and the partial pressures of the components were determined

$$p_1 = \frac{I_1}{I_k^0} \quad p_2 = \frac{I_2}{I_k^0}. \quad (3)$$

The resultant partial pressures were compared with those measured manometrically during preparation of the mixture.

In the case of "ratio" analyses, the instrument was graduated according to a mixture of known composition. In this case, graduation was reduced to finding the relative sensitivity

$$S_{ki} = \frac{I_k^0}{p_k^0} \cdot \frac{p_i^0}{I_i^0}, \quad (4)$$

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where p_k^0 and p_i^0 are the partial pressures of the components of the mixture, while I_k^0 and I_i^0 are the ion currents of the standard mass spectral lines.

A mixture of these same components with a different composition was then admitted to the gas analyzer, its mass spectrum was taken, and the ratio of the partial pressures of the components was determined

$$\frac{p_1}{p_i^0} = \frac{I_2}{I_1} S_{ki}. \quad (5)$$

Before making the analyses, a study was made of conditions for gas leakage from the inlet tank to the ion source and the stability of the sensitivity coefficients x_k and S_{ki} . The adherence to proportionality between the intensity of the mass spectral lines and the pressure of the gas in the "standard"

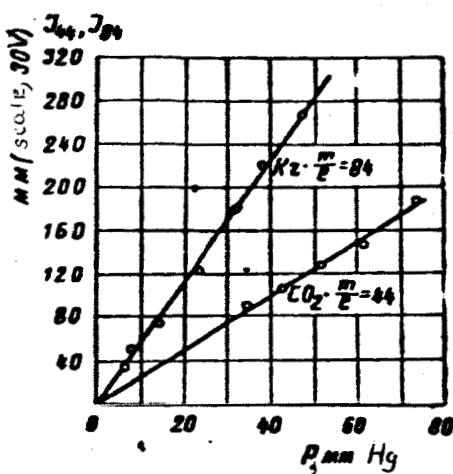


Figure 7. Relationship between intensity of the line $m/e = 84$ for krypton and $m/e = 44$ for carbon dioxide as a function of the pressure of these gases.

volume (fig. 7) indicates that the flux is molecular throughout the entire working pressure range.

As usual, the analysis by ratio is more accurate. The extremely high stability for the coefficients of sensitivity S_{ki} may be seen from data obtained during a week's registration of the spectra for a mixture of methane and carbon dioxide. The mean deviation of S_{ki} from the average value was $\pm 0.9\%$ with a maximum of -1.6% .

Instrumental sensitivity x_k is less stable. Measurements made with carbon dioxide for 5.5 hours showed that the mean deviation of the sensitivity from the average value is $\pm 1.7\%$ with a maximum of -2.5% . Therefore "pressure" graduation should be done immediately before analysis.

As an example, data are given in table 2 from analysis of two mixtures using the "ratio" method.

TABLE 2

Mixture	Composition by manometric measurement	Found by the mass spectrometer method (average of three readings)	Divergence, rel. %
$\text{CO}_2 + \text{CH}_4$	$\text{CO}_2 - 85.3\%$ $\text{CH}_4 - 14.7\%$	$\text{CO}_2 - 85.2\%$ $\text{CH}_4 - 14.8\%$	0.12 0.68
$\text{H}_2 + \text{CH}_4$	$\text{H}_2 - 57\%$ $\text{CH}_4 - 43\%$	$\text{H}_2 - 56.3\%$ $\text{CH}_4 - 43.7\%$	1.23 1.62

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